

1

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CLEANING METHOD FOR INDUSTRIAL SYSTEMS

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The present invention relates generally to an improved method of cleaning industrial equipment, and more specifically to an improved method for treating metal surfaces of industrial equipment with an inorganic acid to remove scale, rust, and other deleterious deposits.

The invention is particularly concerned with, but not limited to the cleaning of internal surfaces of industrial heating systems including boilers, heat exchangers, de-aerating heaters, condensers, storage facilities and connecting lines. During normal operation of this and similar fluid containing equipment, the internal surfaces of the systems become incrustated with relatively insoluble deposits consisting primarily of corrosion products of metals, such as iron, copper and the like, and of insoluble substances depositing from the environment, such as calcium and magnesium salts. As a result, the heating systems must be periodically shut down and the incrustants removed to restore optimum operating efficiency. As will be made more apparent, the conventional cleaning procedures heretofore employed have been time consuming and expensive operations.

Procedures commonly employed for cleaning industrial systems of the type described customarily involve an acidizing treatment in which the incrustated surfaces are acidized by an inhibited inorganic acid, as for example, muriatic acid containing a suitable corrosion inhibitor. In accordance with these conventional procedures, the system to be cleaned is first filled with an acid solution which is allowed to remain in contact with the incrustated surfaces until the dissolving action of the acid ceases, whereupon the bulk of the spent solution containing the dissolved metal salts is directly drained from the system. In actual practice, it frequently is not possible to drain all of the acid solution because of the construction of the system, and it is the removal of this remaining portion of the acid solution without causing the dissolved metal salts to be reprecipitated, together with the need for effectively passivating the freshly cleaned surfaces, which heretofore have been particularly troublesome.

For example, when cleaning boilers, it is known that approximately 1% of the acid solution will be trapped along the bottoms of the headers and drums. Heretofore, it has been the conventional practice to rinse the boilers several times with water by repeatedly filling and draining them in order to dilute the remaining portions of the trapped acid solution. After the acid is essentially all removed by rinsing, the boilers have been then filled with a suitable alkaline solution to completely neutralize the acid and to passivate the freshly pickled metal surfaces, thereby preventing excessive after-rusting. The alkaline solution has been boiled at a pressure up to one-half the operating pressure of the boiler for several hours to restore a desired amount of oxide film on the internal surfaces of the boiler, whereupon the boiler was cooled, again drained out, and finally inspected.

In carrying out the conventional cleaning procedures, it has not been feasible to introduce the alkaline solution into the system being cleaned immediately after draining the bulk of the acid solution, since the dissolved salts in the remaining portion of the acid solution would be reprecipitated as a gelatinous sludge. As a result, the several intermediate rinsing steps have been considered necessary even though the rinsing operations have necessitated inordinately long down-times of the equipment being cleaned. In many applications, the conventional

2

practice also has been undesirably expensive inasmuch as it has been necessary to blanket the equipment with an inert gas during each draining operation to effectively prevent after-rust. For example, when cleaning utility boilers, it has been necessary to introduce an inert gas into the boiler during each rinsing stage to protect the freshly cleaned surfaces from exposure to air, the gas being subsequently exhausted to waste each time the boiler was refilled with water and when it was finally filled with the alkaline solution.

An object of the present invention is to provide an improved method for expeditiously removing relatively insoluble incrustants formed on metal surfaces of industrial equipment.

A more specific object of the invention is to provide an improved method for efficiently removing scale, rust, and similar deposits from the internal surfaces of industrial heating systems.

Still another object of the invention is the provision of a method for treating metal surfaces of industrial equipment with an inorganic acid to remove relatively insoluble incrustations encountered during normal operation by a procedure which avoids the time-consuming rinsing operation of the prior art.

According to the method comprising the present invention, the incrustated metal surfaces to be cleaned are treated in the customary manner with an inhibited acid solution which is retained in contact with the deposits until they are removed. Suitable acid solutions for accomplishing this removal of the deposits are well known in the art, and, in general, are selected depending upon the character of the incrustants. However, an aqueous solution of hydrochloric acid having an HCl content of from 5 to 25 percent has been found particularly effective in cleaning industrial heating equipment and, therefore, the use of such an acid solution is preferred. It is desirable to add to the solution a suitable corrosion inhibitor for the purpose of reducing the attack of the acid solution on the metal surfaces being cleaned.

The length of time required for removing the incrustants will vary depending upon the rate and effectiveness with which the acid attacks the deposits; however, the solution preferably is allowed to remain in the system until the dissolving action of the acid ceases. The speed with which the acid solution acts may be increased in most instances by heating it to an elevated temperature, as for example, approximately 120° to 160° F. or more, when employing the preferred muriatic acid solution.

When the acidizing treatment has been completed, as much as possible of the spent solution is drained from the system and it is immediately filled with a relatively high pH alkaline solution, such as caustic soda, soda ash, trisodium phosphate or the like, dissolved in water. The degree of basicity of the alkaline solution need only be sufficiently great to effect a neutralization of the acid solution which remains in the system after the draining operation, a concentration of about 1% of the alkali having been found sufficient in most instances.

In accordance with the preferred practice of the present invention, the aqueous alkaline solution, which is added to the system immediately after the acidizing treatment, contains sufficient amounts of suitable sequestering or chelating agents selected to form alkali soluble complexes with the metal ions of the dissolved incrustants. The action of the selected sequestering agents advantageously prevents the dissolved salts in the acid solution which remains in the system after draining from precipitating as a gelatinous sludge during the neutralizing operation. As a consequence, the alkaline solution may be added after the bulk of the inhibited acid is removed without the time-consuming, intermediate rinsing steps heretofore considered necessary. When the alkaline solution

3

is subsequently drained from the system, the remaining traces of the dissolved incrustants will be effectively removed.

Another important advantage resulting from the method of the invention is the elimination of the need for an inert gas blanket, as well as other precautions, which has been conventionally used in many applications to prevent oxidation of the clean metal surfaces by exposure to air. To the extent that an undesirable oxide film forms on the clean metal surfaces when the acid solution is drained from the system, these oxides will be dissolved during exposure to the alkaline and sequestering solution. The redissolving of such oxide films may be accelerated by heating the alkaline solution until the metal surfaces are again clean.

The sequestering and chelating agents incorporated in the alkaline solution may be either inorganic or organic materials, although organic materials are preferred. Suitable organic materials include amines, such as glycine, ethylene, diamine, triethanolamine, etc.; polycarboxylic acids and salts, such as citric acid, tartaric acid, gluconic acid, sodium gluconate, etc.; polycarboxylic acid compounds, such as ethylene diamine tetraacetic acid; derivatives of such organic materials; and the like. Among the suitable inorganic materials are salts such as condensed phosphates, e.g. pyrophosphates and tripolyphosphates; cyanides; thiocyanates and the like.

The particular sequestering or chelating agent selected will depend in part upon the alkalinity of the solution in which it is incorporated and the particular metal ions which are to be sequestered. However, the sequestering agents which are preferred are compounds containing a polycarboxylic acid or salt groups, such as the gluconates, and the ethylene diamine tetraacetic acid compounds because of their ability to combine with a wide range of metal ions at relatively high pH values, that is, above 11. For example, sodium gluconate is particularly advantageous for combination with ferric, ferrous, cupric, calcium and magnesium ions.

With certain metal ions, for example, cuprous ions, it may be preferable to add additional complexing or oxidizing agents to supplement the primary sequestering agent and minimize the possibility of copper ions being precipitated from the acid solution. The amines, and, in particular, the ethanolamines, and the thiocyanates are particularly suited for this purpose.

Having thus described the general procedure comprising the present invention, reference will now be made to specific examples of its commercial application. It is to be understood, of course, that the following examples are merely illustrative of the practice of invention and that it may be used in applications other than boiler cleaning, e.g. in the cleaning of pipes, etc., wherein metal surfaces of the system involved become periodically fouled by relatively insoluble deposits.

Example 1

A steam generator of a type commonly used in industrial plants and having a volume of 15,000 gallons to normal operating level has become fouled with deposits, thus necessitating its shut-down and cleaning. Because of high make-up requirements and the continuous internal treatment of the boiler feedwater, the deposits are essentially phosphates of calcium and magnesium and a small amount of iron oxides. A representative sampling of the deposits shows the following approximate composition:

	Percent by weight
Calcium phosphates	60
Magnesium phosphate	30
Iron oxides	10

After the generator has been drained and all outlets have been closed, except for a vent near the top of the system and the blow-down line (the lowest drain in the

4

system), the first step is to charge the generator through the blow-down line with 15,000 gallons of an inhibited 5% hydrochloric acid solution. In accordance with conventional practice, the acid solution is mixed with steam when entering the blow-down line so the temperature of the solution in the generator will be about 160° F., the heated acid solution being retained in the generator until the deposits have been dissolved. When this reaction is complete, the approximate composition of the solution is as follows:

	Percent by weight
Ca ⁺⁺	0.6
Mg ⁺⁺	0.3
Fe ⁺⁺	0.1
HCl	3.0

The bulk of the spent acid solution, except for that which adheres to the metal surfaces and remains along the bottoms of the drums and headers, is then drained from the generator through the blow-down line to waste. The amount of solution remaining in the system is usually less than 1% of the volume of the generator, and, in the illustrative example, is approximately 150 gallons or 1300 pounds of solution.

Assuming that 1300 pounds of solution remains in the system, the approximate amounts of acid and dissolved Ca⁺⁺, Mg⁺⁺, and Fe⁺⁺ ions may be calculated to be:

	Pounds
Ca ⁺⁺	7.9
Mg ⁺⁺	3.9
Fe ⁺⁺	1.3
	<hr/> 13.1
HCl	39.0

Following the draining of the bulk of the acid solution, 15,000 gallons or 130,000 pounds of an aqueous solution containing 1% by weight neutralizing agent and ½% by weight sequestering agent is immediately charged into the generator. In this particular example, the pH of the solution is approximately 13 with the neutralizing agent consisting of ½% soda ash and ½% caustic soda, and the sequestering agent consisting of ¼% sodium gluconate and ¼% sodium salt of ethylene diamine tetraacetic acid. The respective quantitative amounts of neutralizing agents and sequestering agent used is 650 pounds of soda ash and 650 pounds of caustic soda or 1300 pounds total, and 325 pounds of gluconate and 325 pounds of the ethylene diamine tetraacetic acid salt or 650 pounds total.

The solution is then heated and boiled for approximately three hours to circulate it through the system and neutralize the remaining acid, with periodic checks being made to determine if the solution is sufficiently basic. Thereupon the generator is drained, cooled and inspected.

With regard to the specific amounts of neutralizing agent and sequestrant which are used, it has been found that five pounds of neutralizing agent per pound of HCl remaining in the generator and 10 pounds of sequestrant per pound of dissolved metal ions are adequate to effect the neutralizing and sequestering action. Thus, in this specific example where there are approximately 39 pounds of HCl and 13.1 pounds of metal ions, 195 pounds of neutralizing agent and 131 pounds of sequestrant are sufficient. However, in view of the fact that it is impossible to accurately measure the amount of acid solution which remains after draining (such amounts of residual solution varying from system to system) and since it frequently occurs that the blow-down line was prematurely closed, it is desirable to use the amounts of neutralizing agent and sequestrant indicated above (1300 pounds and 650 pounds, respectively) even though such amounts usually are greatly in excess of that actually required in most instances.

In summary, the steps followed in the described example are as follows:

- (1) Fill the boiler with acid solution to dissolve deposits
- (2) Drain acid solution
- (3) Refill with aqueous solution of neutralizing agent and sequestrant
- (4) Boil
- (5) Drain, cool and inspect.

The advantages afforded by the foregoing method of the invention over the prior art will be apparent from the following conventional procedure heretofore used in cleaning the same steam generator system:

- (1) Fill the boiler with acid solution
- (2) Drain acid solution
- (3) Fill with rinse water (1 hour)
- (4) Drain (1½ hours)
- (5) Fill with second rinse water (1 hour)
- (6) Drain (1½ hours)
- (7) Fill with solution of neutralizing agent
- (8) Boil
- (9) Drain, cool and inspect.

Thus, by eliminating the rinsing steps 3 through 6 of the conventionally employed practice, the method of the invention has reduced the cleaning time by approximately five hours. Not only does the improved method decrease the man-hours and, hence, expense required, but it effects a corresponding decrease in down-time of the system.

Example 2

This example involves the cleaning of a steam generator of the type used in public utility generating stations, and has a volume of 30,000 gallons to operating level. Because of low make-up requirements and the use of essentially pure water in the system, the deposits are essentially magnetic iron oxide and approximately 10% copper as metallic copper.

As in the case of Example 1, the cleaning is done with an inhibited 5% hydrochloric acid solution which is mixed with steam and charged into the generator through the blow-down line. Because of the determined presence of copper as a constituent of the deposits, precautions are taken to prevent the dissolved copper from re-depositing from the acid solution as leaves and sheets on the steel boiler surfaces. To this end, approximately 0.2% by weight of thiourea is added to the acid solution, as is common practice in the art. As an alternative procedure, it is possible to dissolve the copper with an ammonia solution which is passed through the generator before the acid solution is introduced.

Upon completion of the reaction in the generator, the bulk of the spent acid solution is drained therefrom leaving an estimated 300 gallons or 2500 pounds of solution along the bottoms of headers and drums and adhering to the metal surfaces of the boiler. The approximate amounts of acid and dissolved metal ions trapped in the generator may be calculated to be:

	Pounds
Fe ⁺⁺ -----	18.0
Cu ⁺⁺ -----	2.5
	<u>20.5</u>
HCl -----	87.0

Following the draining of the bulk of the acid solution from the generator system, 30,000 gallons or 250,000 pounds of an aqueous solution containing 1% neutralizing agent and ½% sequestering agent are immediately charged into the generator through the blow-down line. In this particular example, the neutralizing agent consists of 2500 pounds of caustic soda and the sequestering agent consists of 1250 pounds of sodium gluconate. The pH of the solution is approximately 13.

By calculating the actual amounts of neutralizing agent and sequestering agent required on the basis of five and 10 times, respectively, of the remaining HCl and dissolved metal ions, it will be seen that amounts of material added are considerably in excess of that required. As explained in connection with Example 1, such excess is desirable because of the difficulty in determining the exact amount of acid solution trapped in the generator.

The cleaning operation is completed by heating and boiling the neutralizing solution to circulate it through the system, and finally draining, cooling and inspecting the generator.

It should be noted that the sodium gluconate will not effectively sequester any cuprous copper which remains in the generator after the bulk of the acid solution is drained therefrom, and that the copper will precipitate and be dispersed in the alkaline solution as a black flocculent precipitate. In this particular example, however, the amount of copper that could remain is so small that no special sequestrant is needed to keep it in solution. In other instances where greater quantities of cuprous copper are present, a special sequestrant, such as ammonium thiocyanate or a high boiling amine, e.g. triethanolamine, may be used in addition to the primary sequestrant for the purpose of sequestering the dissolved copper ions.

The conventional procedure heretofore used in cleaning the above-described generator system comprised the following steps:

- (1) Fill with inhibited acid solution
- (2) Drain acid solution
- (3) Introduce nitrogen gas into generator during draining of acid to prevent after-rust (2 hours)
- (4) Fill with rinse water while exhausting nitrogen gas to waste (2 hours)
- (5) Drain water and simultaneously blanket with nitrogen gas (2 hours)
- (6) Refill with second rinse water and expel nitrogen gas (2 hours)
- (7) Drain second rinse water and re-blanket with nitrogen gas (2 hours)
- (8) Introduce alkaline solution and expel nitrogen gas (2 hours)
- (9) Boil solution
- (10) Drain, cool and inspect.

As in the case of Example 1, the method of the invention advantageously eliminates the rinsing steps heretofore employed and reduces the total time required for cleaning by approximately 8 hours. In addition, the prescribed use of the inert gas blanketing the system during the several draining stages also is eliminated, thereby effecting a considerable savings in material. To the extent that any of the after-rust forms on the boiler surfaces when the acid solution is drained from the generator, such oxides will be dissolved during exposure to the alkaline and sequestering solution.

In view of the foregoing detailed description, many other applications of the present method than those specifically set forth will be apparent to those skilled in the art. It is therefore to be understood that the invention is to be broadly construed within the scope of the appended claims.

What is claimed is:

1. A multi-stage process for removing water-insoluble deposits from metal surfaces of industrial equipment consisting of the first stage of dissolving the deposits by exposure to an inorganic acid solution containing a corrosion inhibitor and thereafter removing the bulk of the spent acid solution from contact with the metal surfaces, and the second stage of immediately neutralizing any acid solution adhering to the metal surfaces by exposing them to a dilute, aqueous alkaline solution, said alkaline solution containing a sequestering agent for forming alkali soluble complexes with the metal ions of the dissolved deposits, and finally removing the alkaline solution from contact with the metal surfaces.

7

2. The process in accordance with claim 1 wherein said sequestering agent comprises an organic material.

3. A process of cleaning an industrial system subject to accumulations of water-insoluble deposits on the metal surfaces thereof comprising the steps of exposing the deposits to an inorganic acid solution by filling the system with said acid solution, retaining said acid solution in the system until the deposits are dissolved, draining the bulk of the spent acid solution from the system immediately thereafter refilling the system with an alkaline solution to neutralize the metal surfaces and any acid solution remaining therein, said alkaline solution containing a sequestering agent for forming alkali soluble complexes with the metal ions of the dissolved deposits, and finally draining the alkaline solution from the system.

4. The process in accordance with claim 3 wherein said inorganic acid solution comprises an aqueous solution containing from 5 to 25 percent HCl and a corrosion inhibitor, and wherein said alkaline solution has an alkali weight concentration of at least five times the weight of HCl remaining in the system after the bulk of the acid solution has been drained therefrom.

5. The process in accordance with claim 3 wherein the weight concentration of the sequestering agent in the alkaline solution is at least 10 times the weight of the dissolved metal ions.

6. In a process for cleaning a fluid-containing, industrial system subject to accumulation of water-insoluble deposits which consist primarily of corrosion products of metals and metal salts, the steps of filling the system with an aqueous acid solution containing from 5 to 25 percent HCl and a corrosion inhibitor, retaining the acid solution in the system until the deposits are dissolved,

8

draining the bulk of the spent acid solution from the system, immediately thereafter filling the system with an aqueous neutralizing solution having a weight concentration of alkali at least 5 times the weight of HCl remaining in the system, said neutralizing solution containing, a sequestering agent in an amount at least 10 times the weight of dissolved metal ions remaining in the system, heating the neutralizing solution and allowing it to circulate through the system, and thereafter draining the neutralizing solution from the system.

7. The process in accordance with claim 6 wherein said sequestering agent comprises an inorganic salt.

8. The process in accordance with claim 6 wherein said sequestering agent comprises an organic material.

9. The process in accordance with claim 8 wherein said sequestering agent is an amine.

10. The process in accordance with claim 8 wherein said sequestering agent is an aminopolycarboxylic acid compound.

11. The process in accordance with claim 8 wherein said sequestering agent is a polycarboxylic acid salt.

12. The process in accordance with claim 11 wherein said polycarboxylic acid salt is sodium gluconate.

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